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Intermolecular interactions in linear and nonlinear susceptibilities: beyond the local-field approximation

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Reduced equations of motion for material and radiation field variables in a molecular crystal are presented that allow us to calculate linear- and nonlinear-optical susceptibilities, accounting in a systematic way for intermolecular interactions. These equations are derived starting from the multipolar ($\mu \cdot \mathbf{D}$) Hamiltonian, and to second order in the molecular dipole they reduce to the Bloch–Maxwell equations with local-field corrections. The dielectric function obtained through our approach incorporates retarded interactions in a consistent way and is compared with the existing exciton polariton theory, which is based on the minimal coupling ($\mathbf{p} \cdot \mathbf{A}$) Hamiltonian. We find that, unlike with the conventional polariton theory, spontaneous emission is not suppressed in an infinite crystal.

1. INTRODUCTION

Linear- and nonlinear-optical experiments in condensed phases provide a valuable tool for the study of static and dynamic properties of excited states. One of the major problems in the interpretation of such measurements is caused by the important role that intermolecular interactions play in these systems. From a theoretical point of view the response of a medium to electric fields is most conveniently formulated in terms of wave-vector- and frequency-dependent linear and nonlinear susceptibilities, which are the expansion coefficients of the polarization field in terms of the Maxwell electric field.[1–4] Much effort has been spent to calculate these quantities in terms of molecular properties and intermolecular forces. In particular, for the nonlinear susceptibilities most models lack a firm microscopic basis or their validity is limited to a certain class of systems. Our aim is to develop a procedure to describe nonlinear optics in atomic or molecular condensed phases with localized electronic states that, first, systematically accounts for the interactions and dynamic correlations between the constituents and, second, is flexible in the sense that it can easily be applied to a diversity of systems.

An old and well-known method to account for interactions is the local-field[5,6] approximation. In this approach the effect of intermolecular forces is included in an effective local electric field. The problem of calculating the response of an interacting ensemble of molecules to an electromagnetic field is then reduced to the response of isolated molecules interacting with the local field $\mathbf{E}_L$ through an interaction Hamiltonian $-\mu \cdot \mathbf{E}_L$. Here μ denotes the molecular-dipole operator, and the Lorentz relation between the local field and the Maxwell field $\mathbf{E}$ can then be used to calculate the susceptibilities. Nowadays, local-field corrections are an important ingredient in the explanation of the enhancement of higher-order susceptibilities in condensed phases.[7] It is clear, however, that this method does not incorporate the intermolecular interactions and correlations in a systematic way and that no scheme is provided to improve these results.

In crystalline phases many results are obtained from molecular exciton theory.[2,4,8–11] In these models one starts from the eigenmodes of the crystal Hamiltonian, including the intermolecular instantaneous Coulomb interactions, and calculates the response of these eigenmodes to a perturbation by the internal electromagnetic field. An advantage of this method is that the problem of the actual calculation of the eigenmodes does not need to be solved in order to formulate the theory. The diagonalization of the material Hamiltonian may be considered a separate (complicated) problem. A serious drawback of this procedure is, however, that the concept of excitons is limited to crystals; disordered systems, concentrated solutions, molecular aggregates, etc. cannot be treated in this way. Furthermore, this method is limited even for crystals, because at strong radiation–matter coupling not the eigenstates of the crystal but the collective eigenmodes of radiation field and matter (i.e., polaritons) are the elementary excitations.[8,9,11,12] This becomes particularly important if one wants to account for interactions with other degrees of freedom, such as phonons. To include damping of the excited states by phonons, the polaritons, not the excitons, have to be scattered on the lattice vibrations.[13] The susceptibilities then may no longer be considered a purely material property, and the radiation field has to be considered explicitly as a degree of freedom. Strong evidence of the importance of these and other polariton effects was recently provided through some nonlinear-optical experiments involving second-harmonic generation and transient grating in molecular crystals.[14,15]

In a third method one phenomenologically adds a term $-\mu \cdot \mathbf{E}_{\text{ext}}$ to the material Hamiltonian with instantaneous Coulomb forces.[6] This term reflects the interaction with the external electric field. By using response theory, it is then possible to expand the polarization field in terms of $\mathbf{E}_{\text{ext}}$, which yields external susceptibilities as multitime-correlation functions of the molecular-dipole operators. These external susceptibilities depend on the size and shape of the sample, and one works rather with the more fundamental (internal) susceptibilities, which express the polarization in terms of $\mathbf{E}$, and are generally believed to be intensive quantities. The external susceptibilities can be translated to the internal by using the formal relation between $\mathbf{E}_{\text{ext}}$ and $\mathbf{E}$ provided by the Green function of the Maxwell equations.

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The fact that this method forces one to keep track of size and shape dependencies, which cancel only in the last step of the calculation, is a serious drawback. Moreover, this procedure again leaves no room to incorporate polariton effects in crystals. A more rigorous approach involving external fields can be found in Ref. 16, but the result obtained there is formal because it involves Green functions for the combined matter-and-radiation system.

In this paper we concentrate on the calculation of nonlinear-optical processes for a lattice of polarizable absorbers. The method that we use, however, is not limited to crystals and lends itself to generalization toward other types of systems. The general idea behind our method is to derive a set of coupled reduced equations of motion for those material and radiation field variables that are relevant to the definition of susceptibilities. The electromagnetic field is thus explicitly treated as a degree of freedom, and the coupled equations make it possible to account for polariton effects. In treating the time evolution of the system, we use the multipolar Hamiltonian. The proper choice of a Hamiltonian for charges interacting with radiation is a controversial issue that has drawn considerable attention over the years.[17–24] In the multipolar ($\boldsymbol{\mu}\cdot\mathbf{D}$) Hamiltonian, the radiation–matter interaction is in the electric-dipole approximation given by $-\boldsymbol{\mu}\cdot\mathbf{D}$, with $\mathbf{D}$ the electric displacement field. This Hamiltonian can be obtained by a canonical transformation[18–20] from the more fundamental minimal coupling ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian, in which the radiation–matter coupling is of the form $\mathbf{p}\cdot\mathbf{A}+\mathbf{A}^2$, with $\mathbf{p}$ the electronic momentum and $\mathbf{A}$ the vector potential. Intermolecular forces enter both Hamiltonians in a profoundly different way. In the $\boldsymbol{\mu}\cdot\mathbf{D}$ Hamiltonian there are no direct intermolecular interactions at all; instead they are mediated by an exchange of photons. In the $\mathbf{p}\cdot\mathbf{A}$ Hamiltonian, however, instantaneous Coulomb interactions are explicitly present. Of course, on a formal level both Hamiltonians are equivalent, and in fact it has been shown that when intermolecular interactions are neglected, the susceptibilities predicted by them are identical.[2] If one wants to account for interactions between the absorbers, however, one usually has to resort to approximations in order to solve the time evolution of the system. In view of the different ways in which these interactions enter the Hamiltonians, different predictions may then be expected. The main dilemma in the choice of the Hamiltonian may be formulated as follows. In the $\boldsymbol{\mu}\cdot\mathbf{D}$ Hamiltonian the interaction between the radiation field and the matter is more conveniently treated and makes it most suitable for numerical work (e.g., the propagation of Bloch–Maxwell equations), whereas in the $\mathbf{p}\cdot\mathbf{A}$ Hamiltonian it is easier to incorporate intermolecular forces by using physical intuition.

The outline of this paper is as follows. After introducing the Hamiltonian and pertinent quantities in Section 2, we present our reduced equations of motion in Section 3. The derivation of these equations through a projection-operator technique is only briefly outlined, as it has been extensively reported elsewhere.[25] The value of these equations is that they are formally exact, and in practice they allow us to account for intermolecular interactions and correlations in an approximate but systematic way. For the electromagnetic field they exactly coincide with the Maxwell equations, regardless of the approximations made in working out the material equations. The material equations are obtained to second order in the molecular dipole (the coupling constant), and up to that order they coincide with the Bloch equations in the local-field approximation.[26] This means that each molecule behaves according to the optical Bloch equations in which the electric field is replaced by a local field containing the effects of interactions with the other molecules. The important point of our derivation of the Bloch equations is that it is the first term in a systematic expansion and that it shows limitations of the local-field concept arising from the incomplete treatment of correlations. In Section 4 we calculate the dielectric function from our equations, and we compare it with earlier results. Finally, Section 5 contains our conclusions.

2. MICROSCOPIC MODEL AND HAMILTONIAN

We consider a lattice of arbitrary structure with its N sites occupied by identical molecules. We are interested in transitions between two electronic states of these molecules that are well separated from other electronic levels, so that each molecule may be described as a two-level system with transition energy $\hbar\Omega$. The molecules have no diagonal-dipole matrix elements (nonpolar), but they are polarizable, and the transition-dipole matrix element between the two states will be denoted $\boldsymbol{\mu}$. We further assume that this vector has the same orientation in the lattice for all molecules. Higher-order multipole moments will be neglected, so that we basically consider a lattice of point dipoles.

To describe the electromagnetic field, we work in the Coulomb gauge $\nabla\cdot\mathbf{A}=0$, with $\mathbf{A}$ the vector potential. We confine ourselves in this paper to the linear and nonlinear response to transverse electric fields (no excess charge). As explained in Section 1, we use the multipolar Hamiltonian, which in its dipole approximation (exact for point dipoles) reads as[18,20]

$$\hat{H}=\hat{H}_0+\hat{H}_{\rm int}, \tag{1}$$

with

$$\hat{H}_0=\hbar\Omega\sum_m \hat{B}_m^{\dagger}\hat{B}_m+\hbar\sum_{\mathbf{k}\lambda}\omega_k\hat{a}_{\mathbf{k}\lambda}^{\dagger}\hat{a}_{\mathbf{k}\lambda} \tag{2}$$

and

$$\hat{H}_{\rm int}=-\sum_m \hat{\boldsymbol{\mu}}_m\cdot\hat{\mathbf{D}}^{\perp}(\mathbf{r}_m). \tag{3}$$

Throughout this paper an operator is indicated by a caret, e.g., $\hat{0}$. Its expectation value at time t is written as $\langle\hat{0}(t)\rangle$ or simply as $0(t)$. $\hat{H}_0$ is the total unperturbed Hamiltonian of isolated molecules and radiation. $\hat{B}_m$ ($\hat{B}_m^{\dagger}$) is the destruction (creation) operator for an excitation on molecule m, obeying the Pauli anticommutation relations[4]

$$[\hat{B}_m^{\dagger},\hat{B}_n]_+\equiv\hat{B}_m^{\dagger}\hat{B}_n+\hat{B}_n\hat{B}_m^{\dagger}=\delta_{m,n}+2\hat{B}_m^{\dagger}\hat{B}_n(1-\delta_{m,n}). \tag{4}$$

The vacuum dispersion relation is given by $\omega_k=kc$, and $\hat{a}_{\mathbf{k}\lambda}$ ($\hat{a}_{\mathbf{k}\lambda}^{\dagger}$) denotes the destruction (creation) operator of a photon of wave vector $\mathbf{k}$ and polarization λ, where the usual commutation relations apply:

$$[\hat{a}_{\mathbf{k}\lambda},\hat{a}_{\mathbf{k}'\lambda'}^{\dagger}]=\delta_{\mathbf{k},\mathbf{k}'}\delta_{\lambda,\lambda'}$$

and

$$[\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}'\lambda'}] = 0.$$

$\hat{H}_{\text{int}}$ is the interaction Hamiltonian between the matter and the electromagnetic field. The dipole operator $\hat{\boldsymbol{\mu}}_m$ of the mth molecule reads in terms of the basic molecular operators as

$$\hat{\boldsymbol{\mu}}_m = \boldsymbol{\mu}(\hat{B}_m + \hat{B}_m^{\dagger}) \tag{5}$$

because the molecules are assumed to be polarizable but nonpolar. The position of molecule m is given by $\mathbf{r}_m$, and $\hat{\mathbf{D}}^{\perp}(\mathbf{r})$ is the transverse component of the electric displacement field:

$$\hat{\mathbf{D}}(\mathbf{r}) = \hat{\mathbf{E}}(\mathbf{r}) + 4\pi\hat{\mathbf{P}}(\mathbf{r}), \tag{6}$$

with $\hat{\mathbf{E}}$ and $\hat{\mathbf{P}}$ the electric field and the polarization field, respectively. $\hat{\mathbf{P}}$ is of great importance in defining susceptibilities. Note that for our system of point dipoles it is directly related to the molecular-dipole operators:

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_m \hat{\boldsymbol{\mu}}_m \delta(\mathbf{r} - \mathbf{r}_m). \tag{7}$$

In the multipolar Hamiltonian, $\hat{\mathbf{D}}^{\perp}(\mathbf{r})$ is the conjugate momentum to the vector potential $\hat{\mathbf{A}}^{\perp}(\mathbf{r})$ $[=\hat{\mathbf{A}}(\mathbf{r})]$, and these fields read, in second quantization, as

$$\hat{\mathbf{A}}^{\perp}(\mathbf{r}) = \sum_{\mathbf{k},\lambda} \left(\frac{2\pi\hbar c^2}{V\omega_k}\right)^{1/2} (\hat{a}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}_{\mathbf{k}\lambda}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{r}}) \mathbf{e}_{\mathbf{k}\lambda}, \tag{8a}$$

$$\hat{\mathbf{D}}^{\perp}(\mathbf{r}) = i \sum_{\mathbf{k},\lambda} \left(\frac{2\pi\hbar\omega_k}{V}\right)^{1/2} (\hat{a}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} - \hat{a}_{\mathbf{k}\lambda}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{r}}) \mathbf{e}_{\mathbf{k}\lambda}, \tag{8b}$$

where V denotes the volume of the normalization box, which is taken to be equal to the crystal volume and will be sent to infinity in all final results, and $\mathbf{e}_{\mathbf{k}\lambda}$ is the unit polarization vector of mode $\mathbf{k}\lambda$. As mentioned above, the multipolar Hamiltonian does not contain any explicit intermolecular interactions; all interactions are mediated through the radiation field by emission and absorption of transverse photons.

3. REDUCED EQUATIONS OF MOTION

To describe nonlinear-optical processes, we want to derive coupled equations of motion for the expectation values of material and radiation operators. A natural way to obtain such equations is provided by taking the expectation values of the Heisenberg equations of motion for these operators. This procedure, however, will never give in a rigorous way a closed set of equations for a finite number of expectation values. The reason is that the time derivatives of the material operators contain products of material and radiation field operators. These products are new operators for which, in turn, the Heisenberg equations must be derived, which would again yield new products, etc. This procedure will thus yield an infinite hierarchy of coupled equations, as is common in statistical mechanics.[27] An approximate way out of this is to factorize the expectation value of a product into the product of expectation values. This would be an exact procedure if for all times the system's total density operator were a direct product of a radiation and a matter density operator. Although this may indeed be the case for some initial moment (the infinite past), interactions obviously correlate the radiation evolution and the matter evolution, thus making crude factorization an *ad hoc* approximation. The basic idea of factorization is appealing, however, and leads us to consider projection-operator techniques,[28–31] which give the factorization as a lowest-order result but also prescribe, in principle, an exact procedure to incorporate corrections that are due to interactions.

To construct a suitable projection operator, it is useful first to point out the relevant operators, whose expectation values we want to describe exactly. In our case these are the single-molecule operators ($\hat{B}_m, \hat{B}_m^{\dagger}, \hat{B}_m^{\dagger}\hat{B}_m$) and the creation and annihilation operators $\hat{a}_{\mathbf{k}\lambda}$ and $\hat{a}_{\mathbf{k}\lambda}^{\dagger}$ for a certain discrete set of *special modes* $\mathbf{k}\lambda$ only. The motivation to choose this particular set of operators is as follows. The dynamics of nonlinear-optical experiments is often described adequately by using a few modes of the radiation field that obey the macroscopic Maxwell equations.[3] These modes will constitute the special modes. Furthermore, the polarization field, whose expectation value we ultimately want to relate to the expectation value of the special modes of the electric field, is fully determined by the set of single molecule operators $\hat{B}_m$ and $\hat{B}_m^{\dagger}$ [cf. Eqs. (5) and (7)]. For every m, $\hat{B}_m, \hat{B}_m^{\dagger}, \hat{B}_m^{\dagger}\hat{B}_m$, and the trivial identity operator ($\hat{I}$) constitute a complete set of operators. In Ref. 25 we proposed a time-dependent projection operator $P(t)$ based on the ideas of Lax[29] and Willis and Picard,[30] which allows us to derive exact equations of motion for the expectation values of all operators acting on a single molecule or on a special mode. For the exact form of $P(t)$ and its properties, see Ref. 25. Formally, we write $P(t)\hat{\rho}(t) = \hat{\sigma}(t)$, where $\hat{\rho}(t)$ is the total density operator of the matter and radiation field, and for our projection the reduced density operator $\hat{\sigma}(t)$ is a product of density operators for single molecules and single special modes. All other radiation modes are projected onto the vacuum. Starting from the Liouville equation for the total density operator $\hat{\rho}(t)$, we derive, through steps that are standard in projection-operator techniques, reduced equations of motion for the expectation values of the relevant operators. Let $\hat{A}$ denote such an operator. Then we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{A}(t)\rangle = -i\langle\langle\hat{A}^{\dagger}|L|\hat{\sigma}(t)\rangle\rangle - \int_{-\infty}^{t} \mathrm{d}t' \langle\langle\hat{A}^{\dagger}|L_{\text{int}}G(t,t')Q(t')L_{\text{int}}|\hat{\sigma}(t')\rangle\rangle, \tag{9a}$$

with

$$G(t,t') = \exp_+\left[-i\int_{t'}^{t}\mathrm{d}s(L_0 + Q(s)L_{\text{int}})\right]. \tag{9b}$$

Here L is the Liouville operator associated with the total Hamiltonian, $\hbar L\hat{A} \equiv [\hat{H}, \hat{A}]$, and similarly $\hbar L_0\hat{A} = [\hat{H}_0, \hat{A}]$ and $\hbar L_{\text{int}}\hat{A} = [\hat{H}_{\text{int}}, \hat{A}]$. $Q(s) \equiv 1 - P(s)$ denotes the complementary projection, and $\exp_+$ is the time-ordered exponential. Above, we use Liouville-space notation, whereby an ordinary operator $\hat{A}$ is written as a ket$|\hat{A}\rangle\rangle$, and $\langle\langle\hat{A}|\hat{B}\rangle\rangle \equiv \mathrm{Tr}(\hat{A}^{\dagger}B)$ is the scalar product. $\langle\langle\hat{A}|L|\hat{B}\rangle\rangle \equiv \mathrm{Tr}(\hat{A}^{\dagger}L\hat{B})$ is a Liouville-space matrix element.[32]

The first term on the right-hand side of Eq. (9a) will be called the mean-field term, because it describes the behavior of the system as if the individual molecules and radiation

modes evolved in an uncorrelated way, interacting only with one another's averages, i.e., as if $\hat{\rho}(t) = \hat{\sigma}(t)$ at all times. Evaluation of this term is completely equivalent to taking the expectation value of the Heisenberg equation of motion for $\hat{A}$ and factorizing any expectation value of a product of operators into the product of expectation values.

The second term in Eq. (9a) will be called the kernel (term); it gives the exact correction due to correlated evolution. If $L_{\text{int}}\hat{A}$ is a linear combination of single-molecule and (or) single-special-mode operators, it is easily shown that this term rigorously equals zero. In other words the mean-field term then provides the exact equation of motion for $\langle \hat{A}(t) \rangle$. This is equivalent to the fact that the Heisenberg equation of motion for $\hat{A}(t)$ in that case would not contain any operator products that would have to be factorized. In general, however, the kernel term is complicated, and it is impossible to evaluate it without approximations because all the problems of correlated dynamics are hidden in it. The natural way to proceed is to expand $G(t, t')$ perturbatively in the interaction

$$G(t, t') = G_0(t, t') - i \int_{t'}^{t} dt_1 G_0(t, t_1) Q(t_1) L_{\text{int}} G_0(t_1, t') + \dots , \tag{10}$$

where $G_0(t, t') = \exp[-iL_0(t - t')]$ is the unperturbed propagator. Alternatively, a density (cluster) expansion of $G(t, t')$ may be developed.[27] To calculate the kernel term, we have to parameterize $\hat{\sigma}(t)$ in terms of the expectation values of the single-molecule and single-special-mode operators. Formally, this can always be done because of the factorized form of $\hat{\sigma}(t)$. If we then evaluate Eq. (9a) for all single-molecule and single-special-mode operators, we obtain a closed set of equations for their expectation values.

In Ref. 25 the formalism described above has been used to derive explicit reduced equations of motion for our relevant material and field variables. For the radiation variables, these equations do not involve the kernel by virtue of the fact that $L_{\text{int}}\hat{a}_{\mathbf{k}\lambda}$ is a linear combination of single-molecule operators. As noted above, this means that the mean-field terms provide the exact equations of motion for the radiation field variables. We eventually find, for the special $\mathbf{k}$ values, that

$$(k^2 - \omega^2/c^2)\mathbf{E}^{\perp}(\mathbf{k}, \omega) = 4\pi(\omega^2/c^2)\mathbf{P}^{\perp}(\mathbf{k}, \omega), \tag{11}$$

with $\mathbf{E}^{\perp}(\mathbf{k}, \omega)$ [$\mathbf{P}^{\perp}(\mathbf{k}, \omega)$] the time-and-space Fourier transform of the transverse electric field (polarization field). This result proves that the multipolar Hamiltonian in the dipole approximation is *not* incompatible with Maxwell's equations. This conclusion is different from earlier results.[24] Note that in view of the exactness of the mean-field term, the definition of special modes and the introduction of a projection operator are not essential to the above conclusion.

Next, we turn to the equations for the material variables. Instead of $\hat{B}_m$, $\hat{B}_m^{\dagger}$ and $\hat{B}_m^{\dagger}\hat{B}_m$, we choose the linear combinations $\hat{B}_m + \hat{B}_m^{\dagger}$, $i(\hat{B}_m - \hat{B}_m^{\dagger})$ and $\hat{W}_m = \hat{B}_m^{\dagger}\hat{B}_m - \hat{B}_m\hat{B}_m^{\dagger} = 2\hat{B}_m^{\dagger}\hat{B}_m - \hat{I}$ as basic operators. The optical Bloch equations for an isolated two-level molecule, which are frequently used to describe nonlinear-optical processes,[3,33] are usually formulated in terms of these Hermitian operators. Note that the polarization field is directly related to $\hat{B}_m + \hat{B}_m^{\dagger}$, and $\hat{W}_m$ is the population inversion of molecule m. For $\langle \hat{B}_m + \hat{B}_m^{\dagger} \rangle$, the mean-field term is easily shown to be exact again, but for the other two variables the kernel does contribute. In Ref. 25 we calculated this contribution to second order in the interaction, which means that we keep only the first term in Eq. (10). The mean-field term was calculated without approximations. It turns out that the kernel essentially yields the retarded dipolar interactions between the molecules, which is to be expected because the diagrams that contribute to it contain creation and subsequent destruction of a photon at two different molecules. It has been shown before[34,35] that this gives the dipole–dipole interaction. If emission and absorption happen at the same molecule, the diagram contributes to the radiative lifetime and to a level (Lamb) shift; thus the radiative lifetime and the Lamb shift parameters are also properly included in our equations. To second order in the dipole moment μ, the equations for $\hat{B}_m + \hat{B}_m^{\dagger}$, $i(\hat{B}_m - \hat{B}_m^{\dagger})$, and $\hat{W}_m$ can now be written as the Bloch equations for molecule m in a local electric field that consists of the Maxwell field $\mathbf{E}(\mathbf{r}_m)$ and a term due to the retarded dipole interactions with the other molecules.[25] Through the projection procedure outlined above we are thus able to define from first principles a local field in nonlinear optics for systems with interacting molecules. Moreover, our method shows the approximate nature of the local-field approach and provides a tool to improve on it systematically by incorporating higher-order kernel terms. We also note that our equations include superradiance effects because they contain the complete complex dipole–dipole interactions [cf. Eq. (15a)]. When we define, in analogy with the polarization $\hat{\mathbf{P}}(\mathbf{r})$, the material fields $\hat{\mathbf{V}}(\mathbf{r}) = \sum_m i\boldsymbol{\mu}(\hat{B}_m - \hat{B}_m^{\dagger})\delta(\mathbf{r} - \mathbf{r}_m)$, $\hat{W}(\mathbf{r}) = \sum_m \hat{W}_m\delta(\mathbf{r} - \mathbf{r}_m)$, and $\rho(\mathbf{r}) = \sum_m \delta(\mathbf{r} - \mathbf{r}_m)$ (the molecular number density), the set of reduced equations of motion in the local-field approximation reads, in $(\mathbf{k}, \omega)$ representation ($\mathbf{k}$ in the special set), as[25]

$$-i\omega\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle = -\Omega\langle \hat{\mathbf{V}}(\mathbf{k}, \omega) \rangle - \Gamma\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle, \tag{12a}$$

$$\begin{aligned} -i\omega\langle \hat{\mathbf{V}}(\mathbf{k}, \omega) \rangle = {} & \Omega\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle - [\Gamma + K_1(\omega)]\langle \hat{\mathbf{V}}(\mathbf{k}, \omega) \rangle \\ & + \frac{2}{\hbar}\boldsymbol{\mu}\boldsymbol{\mu} \cdot \frac{1}{2\pi V} \sum_{k'}^{\text{1BZ}} \int d\omega' \mathbf{E}_L(\mathbf{k}', \omega') \\ & \times \langle \hat{W}(\mathbf{k} - \mathbf{k}', \omega - \omega') \rangle, \end{aligned} \tag{12b}$$

$$\begin{aligned} -i\omega\langle \hat{\mathbf{W}}(\mathbf{k}, \omega) \rangle = {} & -\tfrac{1}{2}K_2(\omega)[2\pi\rho(\mathbf{k})\delta(\omega) + \langle \hat{W}(\mathbf{k}, \omega) \rangle] \\ & + \tfrac{1}{2}K_3(\omega)[2\pi\rho(\mathbf{k})\delta(\omega) - \langle \hat{W}(\mathbf{k}, \omega) \rangle] \\ & - \frac{2}{\hbar}\frac{1}{2\pi V} \sum_{k'}^{\text{1BZ}} \int d\omega' \mathbf{E}_L(\mathbf{k}', \omega') \\ & \cdot \langle \hat{\mathbf{V}}(\mathbf{k} - \mathbf{k}', \omega - \omega') \rangle. \end{aligned} \tag{12c}$$

Here, $\boldsymbol{\mu}\boldsymbol{\mu}$ stands for the tensor with ijth component $\mu_i\mu_j$ (dyad), and 1BZ denotes that the summation extends over the first Brillouin zone of the reciprocal lattice only. In Eqs. (12), Γ accounts for pure dephasing (T_2 processes) in a phenomenological way, and the K_i are the self-interaction kernels responsible for radiative decay (γ_i) and level shifts (Δ_i). We have

$$K_1(\omega) = \lim_{\epsilon \downarrow 0} \frac{4\mu^2}{3\hbar\pi} i \int dk\, k^3 \left(\frac{1}{\tilde{\omega} + k + i\epsilon} + \frac{1}{\tilde{\omega} - k + i\epsilon} \right)$$

$$\equiv \gamma_1(\omega) + i\Delta_1(\omega), \tag{13a}$$

with $\tilde{\omega} \equiv \omega/c$. The expressions for $K_2(\omega)$ and $K_3(\omega)$ are obtained from $K_1(\omega)$ by replacing k in the denominators with $k - \Omega/c$ and $k + \Omega/c$, respectively. The frequency-dependent decay rates $\gamma_i(\omega)$ agree with those obtained through other methods,[33] and in explicit form they read as

$$\gamma_1(\omega) = (4\mu^2/3\hbar c^3)|\omega|^3, \tag{13b}$$

$$\gamma_2(\omega) = \frac{4\mu^2}{3\hbar c^3} \begin{cases} (\omega + \Omega)^3 & (\omega > \Omega) \\ (\omega + \Omega)^3 + (\Omega - \omega)^3 & (-\Omega < \omega < \Omega) \\ (\Omega - \omega)^3 & (\omega < -\Omega) \end{cases}, \tag{13c}$$

$$\gamma_3(\omega) = \frac{4\mu^2}{3\hbar c^3} \begin{cases} (\omega - \Omega)^3 & (\omega > \Omega) \\ 0 & (-\Omega < \omega < \Omega) \\ -(\omega + \Omega)^3 & (\omega < -\Omega) \end{cases}. \tag{13d}$$

The divergent level shifts $\Delta_i(\omega)$ are not equal to the usual Lamb shift obtained within the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian. This is due to the fact that a real self-interaction term,

$$2\pi \int d\mathbf{r} \sum_m |\hat{\mathbf{P}}_m{}^{\perp}(\mathbf{r})|^2,$$

where $\hat{\mathbf{P}}_m{}^{\perp}$ is the transverse polarization field due to molecule m only, has been omitted from the Hamiltonian [Eq. (1)] by us. It has been shown that for the hydrogen atom this term exactly resolves the discrepancy in the Lamb shift.[20] For our model of two-level systems, however, the extra term is an infinite constant that cannot affect the dynamics. The two-level approximation is apparently too severe an approximation to deal with all self-interactions in an exact way.

We now turn to the discussion of the most important quantity in Eqs. (12), the local field in $(\mathbf{k}, \omega)$ representation, which reads as

$$\mathbf{E}_L(\mathbf{k}, \omega) = \langle \hat{\mathbf{E}}^{\perp}(\mathbf{k}, \omega) \rangle + (4\pi/3)\boldsymbol{\eta}(\mathbf{k}, \omega) \cdot \langle \mathbf{P}(\mathbf{k}, \omega) \rangle, \tag{14a}$$

with the tensor $\boldsymbol{\eta}(\mathbf{k}, \omega)$ given by

$$\boldsymbol{\eta}(\mathbf{k}, \omega) = \mathbf{1} - 3\hat{\mathbf{k}}\hat{\mathbf{k}} + (3/4\pi)[\mathbf{F}_l(\mathbf{k}, \omega) - \mathbf{F}_c(\mathbf{k}, \omega)]. \tag{14b}$$

Here $\mathbf{F}_l(\mathbf{k}, \omega)$ and $\mathbf{F}_c(\mathbf{k}, \omega)$ are the lattice and continuous-space Fourier transforms of the retarded dipole field tensor $\mathbf{F}(\mathbf{r}, \omega)$, respectively[34,36]:

$$\mathbf{F}(\mathbf{r}, \omega) = \{(3 - 3i\tilde{\omega}r - (\tilde{\omega}r)^2)\hat{\mathbf{r}}\hat{\mathbf{r}} - [1 - i\tilde{\omega}r - (\tilde{\omega}r)^2]\mathbf{1}\} \frac{e^{i\tilde{\omega}r}}{r^3}, \tag{15a}$$

$$\mathbf{F}_l(\mathbf{k}, \omega) = \frac{1}{\rho} \sum_{m \neq 0} \mathbf{F}(\mathbf{r}_m, \omega) \exp(-i\mathbf{k} \cdot \mathbf{r}_m), \tag{15b}$$

$$\mathbf{F}_c(\mathbf{k}, \omega) = \int d\mathbf{r} \mathbf{F}(\mathbf{r}, \omega) e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{15c}$$

$\hat{\mathbf{k}}$ and $\hat{\mathbf{r}}$ denote unit vectors in the $\mathbf{k}$ and $\mathbf{r}$ directions, respectively, and $\rho \equiv N/V$ is the average number density of the molecules. The fact that $\boldsymbol{\eta}(\mathbf{k}, \omega)$ contains the difference of the discrete and continuous Fourier transform of the same field is a result of the proper bookkeeping of intermolecular interactions, which is maintained by the projection operator. Strictly speaking, the Maxwell field $\langle \hat{\mathbf{E}}(\mathbf{k}, \omega) \rangle$ already contains some contributions from intermolecular interactions, and the subtraction of $\mathbf{F}_c(\mathbf{k}, \omega)$ avoids overcounting the interactions. Furthermore, the difference $\mathbf{F}_l - \mathbf{F}_c$ is most suitable for numerical evaluation because only a small region in space contributes to it, as the summation of Eq. (15b) and integration of Eq. (15c) are identical at large distances r. Moreover, it can be shown that for a simple cubic lattice with lattice spacing a in the limit $k \to 0$ $(ka \ll 1)$ *and* $\omega \to 0$ $(\tilde{\omega}a \ll 1)$, $\mathbf{F}_l = \mathbf{F}_c$ (cf. Section 4), so that

$$\boldsymbol{\eta}(\mathbf{k}, \omega) = \mathbf{1} - 3\hat{\mathbf{k}}\hat{\mathbf{k}} \qquad (k, \omega \to 0). \tag{16}$$

In Eq. (14a) we expressed the local field in terms of $\mathbf{E}^{\perp}$ and $\mathbf{P}$ because $\mathbf{E}^{\perp}$ is the transverse Maxwell field with respect to which we will define susceptibilities. In principle, we may equally well write $\mathbf{E}_L = \mathbf{E} + (4\pi/3)\boldsymbol{\eta}' \cdot \mathbf{P}$, and then $\boldsymbol{\eta}'$ would be given by Eq. (14b) without the $\hat{\mathbf{k}}\hat{\mathbf{k}}$ term. Thus, in the limit $k, \omega \to 0$, we find exactly the Lorentz local field $\mathbf{E} + (4\pi/3)\mathbf{P}$.

In concluding this section we note how Eqs. (12) may be used to derive expressions for molecular-optical susceptibilities. To that end we formally expand the material variables $\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle$, $\langle \hat{\mathbf{V}}(\mathbf{k}, \omega) \rangle$, and $\langle \hat{W}(\mathbf{k}, \omega) \rangle$ in a Taylor series in $\mathbf{E}_L(\mathbf{k}, \omega)$. When these expansions are substituted into Eqs. (12), we can obtain the coefficients of expansion of the material variables order by order. The coefficients of expansion of $\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle$ constitute the molecular susceptibilities. Because Eqs. (12) are equivalent to the Bloch equations of a single molecule interacting with the field $\mathbf{E}_L$, these are actually the molecular polarizabilities. (This is no longer true once the kernel is evaluated to higher orders.) The macroscopic susceptibilities are defined in terms of the expansion of $\langle \hat{\mathbf{P}}(\mathbf{k}, \omega) \rangle$ in a power series in the average Maxwell field $\mathbf{E}$ rather than the local field $\mathbf{E}_L$. Using the relation between $\mathbf{E}$ and $\mathbf{E}_L$ [Eq. (14a)], we can expand $\mathbf{E}_L$ in powers of $\mathbf{E}$ and obtain the macroscopic susceptibilities.[2,6,26] The macroscopic susceptibility to order n is then given by sums of products of the molecular susceptibilities of order n and lower. It should further be noted that in this approximation we can express the susceptibilities in terms of correlation functions of the matter, as is common in linear and nonlinear response theory.[37] In Section 4 we explicitly evaluate the linear susceptibility and the dielectric function for the present model and compare them with other results.

4. COMPARATIVE STUDY OF THE DIELECTRIC FUNCTION

The Bloch equations [Eqs. (12)] can be used in a straightforward way to calculate the linear susceptibility $\boldsymbol{\chi}^{(1)}(\mathbf{k}, \omega)$. This tensor is defined by

$$\langle \hat{\mathbf{P}}^{(1)}(\mathbf{k}, \omega) \rangle = \boldsymbol{\chi}^{(1)}(\mathbf{k}, \omega) \cdot \langle \hat{\mathbf{E}}^{\perp}(\mathbf{k}, \omega) \rangle, \tag{17}$$

where $\langle \hat{\mathbf{P}}^{(1)}(\mathbf{k}, \omega) \rangle$ denotes that part of the polarization that is linear in the electric field. Because we consider only transverse radiation fields, it should actually be referred to as the transverse susceptibility. The (transverse) dielectric

function $\epsilon(\mathbf{k}, \omega)$ is often considered instead of the susceptibility and is defined by

$$\epsilon(\mathbf{k}, \omega) = 1 + 4\pi\chi^{(1)}(\mathbf{k}, \omega). \tag{18}$$

To obtain the linear susceptibility, we linearize the Bloch equations by discarding all terms of second or higher order in the expectation value of the electric field. Because the molecules are nonpolar, $\langle \hat{\mathbf{P}}(\mathbf{k}, \omega)\rangle$ and $\langle \hat{\mathbf{V}}(\mathbf{k}, \omega)\rangle$ both vanish in the absence of electric fields, so that in lowest order they are linear in $\langle \hat{\mathbf{E}}^{\perp}(\mathbf{k}, \omega)\rangle$. To find the behavior of $\langle \hat{W}(k, t)\rangle$, we realize that the inversion $\langle \hat{W}_m(t)\rangle$ of molecule m is -1 in the absence of fields because the molecule is in the ground state. As it takes two interactions with the electromagnetic field to change the ground-state density operator $|0\rangle_{mm}\langle 0|$ for molecule m into the excited state $|1\rangle_{mm}\langle 1|$, the next term in the expansion of $\langle \hat{W}_m(t)\rangle$ will be quadratic in the electric field. Linearizing the Bloch equations is thus equivalent to invoking

$$\langle \hat{W}(\mathbf{k}, \omega)\rangle = 2\pi\delta(\omega) \sum_m (-1)\exp(-i\mathbf{k}\cdot\mathbf{r}_m)$$

$$= -2\pi\delta(\omega)N \sum_{\mathbf{G}} \delta_{\mathbf{k},2\pi\mathbf{G}}, \tag{19}$$

where the summations over m and $\mathbf{G}$ run over the total crystal and the reciprocal lattice, respectively, and N, again, denotes the total number of molecules in the system. It is readily checked that Eq. (12c) is now indeed obeyed up to terms linear in the transverse electric field, as $K_3(0) = 0$. Using the expression for the local field [Eq. (14)], we now obtain, as linear equations,

$$-i\omega\langle \hat{\mathbf{P}}(\mathbf{k}, \omega)\rangle = -\Omega\langle \hat{\mathbf{V}}(\mathbf{k}, \omega)\rangle - \Gamma\langle \hat{\mathbf{P}}(\mathbf{k}, \omega)\rangle, \tag{20a}$$

$$-i\omega\langle \hat{\mathbf{V}}(\mathbf{k}, \omega)\rangle = [\Omega - (8\pi/3\hbar)\rho\mu^2\eta(\mathbf{k}, \omega)]\langle \hat{\mathbf{P}}(\mathbf{k}, \omega)\rangle - [\Gamma + K_1(\omega)]\langle \hat{\mathbf{V}}(\mathbf{k}, \omega)\rangle - (2/\hbar)\,\rho\boldsymbol{\mu}\boldsymbol{\mu}\cdot\langle \hat{\mathbf{E}}^{\perp}(\mathbf{k}, \omega)\rangle, \tag{20b}$$

where the superscript 1's denoting the linear parts of $\mathbf{P}$ and $\mathbf{V}$ have been omitted for brevity. Furthermore, we introduce the scalar

$$\eta(\mathbf{k}, \omega) \equiv [\boldsymbol{\mu}\cdot\boldsymbol{\eta}(\mathbf{k}, \omega)\cdot\boldsymbol{\mu}]/\mu^2, \tag{21}$$

and we use the fact that the polarization field is collinear with $\boldsymbol{\mu}$ in identifying

$$\boldsymbol{\mu}\boldsymbol{\mu}\cdot\boldsymbol{\eta}\cdot\langle \hat{\mathbf{P}}(\mathbf{k}, \omega)\rangle = \boldsymbol{\mu}\cdot\boldsymbol{\eta}\cdot\boldsymbol{\mu}\langle \hat{\mathbf{P}}(\mathbf{k}, \omega)\rangle. \tag{22}$$

The dielectric function is now obtained by eliminating $\langle \hat{\mathbf{V}}(\mathbf{k}, \omega)\rangle$ from Eqs. (20) and reads as

$$\frac{\epsilon(\mathbf{k}, \omega) - 1}{4\pi} = \frac{2\rho\Omega\mu\mu/\hbar}{-(\omega + i\Gamma)[\omega - \Delta_1(\omega) + i\Gamma + i\gamma_1(\omega)] + \Omega[\Omega - (8\pi/3\hbar)\rho\mu^2\eta(\mathbf{k}, \omega)]}, \tag{23}$$

We compare our result with the dielectric function as obtained by Hopfield in his celebrated treatment of the polariton.[12] This result is derived within the minimal coupling ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian, and in the original paper it is defined through the dispersion relation of the mixed eigenmodes of the matter and radiation operators. The same result is found by evaluating only the Heisenberg equations of motion for $(\hat{B}_m + \hat{B}_m^{\dagger})$, $i(\hat{B}_m - \hat{B}_m^{\dagger})$, and $\hat{W}_m$ within the ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian, taking the expectation values of those equations while factorizing all products (which is equivalent to taking only the mean-field term in our projection approach), and linearizing the resulting equations as explained above. We then find that

$$\frac{\epsilon_{\min}(\mathbf{k}, \omega) - 1}{4\pi} = \frac{2\rho\Omega\mu\mu/\hbar}{-\omega^2 + \Omega[\Omega - (8\pi/3\hbar)\rho\mu^2\eta_{\min}(\mathbf{k})]}, \tag{24}$$

with

$$\eta_{\min}(\mathbf{k}) = -(3/4\pi)[\hbar J_0(\mathbf{k})/\rho\mu^2]. \tag{25}$$

$J_0(\mathbf{k})$ is defined as the lattice Fourier transform of the instantaneous dipole–dipole interaction:

$$J_0(\mathbf{k}) = \sum_{m\neq 0} J(\mathbf{r}_m)\exp(-i\mathbf{k}\cdot\mathbf{r}_m), \tag{26a}$$

with

$$\hbar J(\mathbf{r}) = \boldsymbol{\mu}\cdot(1 - 3\hat{\mathbf{r}}\hat{\mathbf{r}})(1/r^3)\cdot\boldsymbol{\mu} = -\boldsymbol{\mu}\cdot\mathbf{F}(\mathbf{r}, \omega = 0)\cdot\boldsymbol{\mu} \tag{26b}$$

[cf. Eq. (15a)]. Clearly, Eqs. (23) and (24) differ. Let us discard the dephasing in our result because it can also be incorporated into Eq. (24). A striking and important discrepancy between Eqs. (23) and (24) is the presence of self-interactions (spontaneous emission and Lamb shift) in the first. Hopfield concluded that spontaneous emission is suppressed in an infinite crystal and that the electromagnetic field coupled to the polarization wave (polariton) propagates freely. In contrast, our result using the multipolar Hamiltonian does contain spontaneous emission. A further difference is that Hopfield's expression does not contain retarded interactions between the molecules; our result does. This is seen most clearly by comparing $\eta(\mathbf{k}, \omega)$ with $\eta_{\min}(\mathbf{k})$. [The fact that $\eta_{\min}(\mathbf{k})$ depends only on $\mathbf{k}$ already rules out any signature of retarded interactions.]

We will now make a more quantitative study of the different expressions for the dielectric function, in which we specifically investigate the role of the (retarded) intermolecular interactions. To this end, from now on we will neglect the dephasing and self-interaction contributions to Eq. (23), and, for simplicity, we will confine ourselves to the case of an electric field polarized parallel to the molecular-transition dipoles. This special geometry allows us to ignore the tensor nature of the studied quantities, which is not essential for the discussion. To make a quantitative comparison, we have to evaluate the lattice sums of the retarded and the instantaneous dipole interactions as occurring in Eqs. (15b) and (26a). Although sophisticated schemes have been developed to obtain these sums,[38] here we use a simple approximation, which yields the $k = 0$, $\omega = 0$ result and the first nontrivial terms depending on k and ω. In this approximation, used by Heller and Marcus to derive the effective mass of the dipolar exciton,[39] the lattice sum is replaced by an integral over all space, excluding an inner sphere with cutoff radius R_c, which is of the order of the lattice constant. One thus finds for the instantaneous interaction (in our geometry) that[39,40]

$$\hbar J_0(\mathbf{k}) \approx -(4\pi/3)\mu^2\rho[j_0(kR_c) + j_2(kR_c)], \quad (27)$$

with $j_0(x)$ and $j_2(x)$ the zeroth- and second-order spherical Bessel functions of the first kind, respectively.[41] Keeping only terms up to second order in kR_c, which is of the order of 0.001 for optical wavelengths, and using Eq. (25), we have

$$\eta_{\min}(k) \approx 1 - \tfrac{1}{10}(kR_c)^2. \quad (28)$$

The summation of the retarded dipole-field tensor $\mathbf{F}$ is simplified considerably by the fact that only the difference of the lattice and the continuous space Fourier transform occur in Eq. (14b). In the integral approximation for the lattice sum this difference now amounts to the integral of $\mathbf{F}$ over the inner sphere:

$$\Delta\mathbf{F}(\mathbf{k}, \omega) = \mathbf{F}_l(\mathbf{k}, \omega) - \mathbf{F}_c(\mathbf{k}, \omega) \approx -\int_0^{R_c} \mathbf{F}(\mathbf{r}, \omega)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}. \quad (29)$$

Using Eq. (15a) for $\mathbf{F}(\mathbf{r}, \omega)$ and performing the angular integrals of $\mathbf{r}$ first, we end up with integrals over $|\mathbf{r}|$ involving spherical Bessel functions, which cannot be evaluated analytically. However, because the integral extends only over small $|\mathbf{r}|$ values ($kR_c \ll 1$, $\tilde{\omega}R_c \ll 1$), we may expand the Bessel functions in powers of $|\mathbf{r}|$ to obtain the first terms in an expansion of $\Delta\mathbf{F}(\mathbf{k}, \omega)$ in powers of kR_c and $\tilde{\omega}R_c$. We eventually find, for our special geometry and by using Eqs. (14b) and (21), that

$$\eta(k, \omega) \approx 1 - \tfrac{1}{10}(kR_c)^2 - (\tilde{\omega}R_c)^2. \quad (30)$$

We immediately note that for $\tilde{\omega} = 0$, expression (30) reduces to expression (28), which means that if we neglect the retardation in the molecular interactions our result is equal to Hopfield's, except for the role of spontaneous emission.

To estimate the effect of retardation further, we now write the dielectric function in the following form suggested by exciton theory (only one exciton branch considered)[10]:

$$\frac{\epsilon(k, \omega) - 1}{4\pi} = \frac{C}{-\beta\omega^2 + \bar{\Omega}^2 + \dfrac{\hbar\bar{\Omega}}{m^*}k^2}. \quad (31)$$

Here $\Omega_{ex}^2(k) = \bar{\Omega}^2 + (\hbar\bar{\Omega}/m^*)k^2$ is usually the long-wavelength dispersion relation of the transverse Coulomb exciton, and m^* is its effective mass. The parameters C, β, $\bar{\Omega}$, and m^* for the dielectric functions discussed above are shown in Table 1. For both models we find that $\bar{\Omega}$ and m^* equal the $k = 0$ frequency and the effective mass, respectively, of the transverse dipolar exciton (without invoking the Heitler–London approximation).[4,11,39] The effect of retardation is fully reflected in β. For $\epsilon_{\min}$, $\beta = 1$, as one expects, because this result can be obtained by first diagonalizing the material Hamiltonian, which gives the dipolar excitons, and then applying response theory to a perturbation of the exciton Hamiltonian by a $\mathbf{p} \cdot \mathbf{A}$ interaction with the radiation field. Considering the excitons as harmonic oscillators, with k-dependent frequency $\Omega_{ex}(k)$, which is valid in the linear approximation, one expects a resonance in the susceptibility at $\omega = \Omega_{ex}(k)$. Our result [Eq. (23)] may not be obtained by such a consideration because in the multipolar Hamiltonian the transverse radiation field is essential to carry the intermolecular interactions; if we want to take these into account, the material system may not be considered a separate entity, which is perturbed by the radiation. Still, our result also has many of the instantaneous exciton characteristics. Only the fact that $\beta \neq 1$ shows the influence of retardation and may be interpreted as an effective resonance shift. Typical values for the microscopic parameters ($\Omega \approx 10^{15}$ sec^{-1}, $\mu \approx 1$ D, $R_c \approx 1$ Å, and $\rho R_c^3 \approx 1$) give $1 - \beta \approx 10^{-6}$, which illustrates that for realistic samples the role of retardation in the dielectric function is negligible. The same conclusion was reached by Davydov.[4]

Also shown in Table 1 are the parameters C, β, $\bar{\Omega}$, and m^* for simplifications of both models discussed here. In the case $\mathbf{p} \cdot \mathbf{A}$ bare we consider Hopfield's result without dipolar interactions, i.e., $J_0(\mathbf{k}) = 0$. Clearly, the susceptibility of a sample of noninteracting molecules is the density times the single molecule polarizability. We see that, indeed, the resonance frequency is given by the molecular transition frequency and the effective mass is infinite because of the absence of distance-dependent interactions. The case $\boldsymbol{\mu} \cdot \mathbf{D}$ bare corresponds to our equation-of-motion approach omitting the kernel term. Now, the resonance frequency is not the molecular frequency because the field with which each molecule interacts is the displacement $\mathbf{D}$ instead of $\mathbf{E}$, which means that there is a local field $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$, corresponding (for the transverse geometry) to $\eta \equiv \bar{\eta} = 3$ in Eq. (14a). This nontrivial local field shifts the resonance. It does not, however, introduce a finite effective mass: $\bar{\eta}$ has no k dependence.

Finally, we note that performing response theory on a perturbation of Coulomb excitons by adding a $\boldsymbol{\mu} \cdot \mathbf{E}$ interaction with the radiation field (which is a fourth method to calculate susceptibilities) exactly yields Hopfield's results.

Table 1. Parameters C, β, $\bar{\Omega}$, and m^* Needed to Express the Dielectric Functions Discussed in the Text in the Form of Eq. (31)[a]

Model	C	β	$\bar{\Omega}$	$(m^*)^{-1}$
$\boldsymbol{\mu} \cdot \mathbf{D}$ [Eq. (23)]	$\dfrac{2\rho\Omega\mu^2}{\hbar}$	$1 - \dfrac{8\pi\rho\Omega\mu^2R_c^2}{3\hbar c^2}$	$\left[\Omega\left(\Omega - \dfrac{8\pi\rho\mu^2}{3\hbar}\right)\right]^{1/2}$	$\dfrac{\Omega}{\bar{\Omega}}\dfrac{4\pi\rho\mu^2R_c^2}{15\hbar^2}$
$\mathbf{p} \cdot \mathbf{A}$ [Eq. (24)]	$\dfrac{2\rho\Omega\mu^2}{\hbar}$	1	$\left[\Omega\left(\Omega - \dfrac{8\pi\rho\mu^2}{3\hbar}\right)\right]^{1/2}$	$\dfrac{\Omega}{\bar{\Omega}}\dfrac{4\pi\rho\mu^2R_c^2}{15\hbar^2}$
$\boldsymbol{\mu} \cdot \mathbf{D}$ bare	$\dfrac{2\rho\Omega\mu^2}{\hbar}$	1	$\left[\Omega\left(\Omega - \dfrac{8\pi\rho\mu^2}{\hbar}\right)\right]^{1/2}$	0
$\mathbf{p} \cdot \mathbf{A}$ bare	$\dfrac{2\rho\Omega\mu^2}{\hbar}$	1	Ω	0

[a] $\rho \equiv N/V$ is the number density, Ω is the molecular transition frequency, μ is the transition dipole, and R_c is of the order of the lattice constant. The parameters may alternatively be expressed in terms of the oscillator strength per unit volume, $(2M\Omega\rho\mu^2)/\hbar e^2$, with M and e the electron mass and charge, respectively. The discrepancy of the first two models regarding spontaneous emission is not included in this table.

5. CONCLUDING REMARKS

The systematic incorporation of intermolecular forces into the theory of linear- and nonlinear-optical processes in condensed phases is an important problem. In this paper we approached the problem by using reduced equations of motion, which describe the evolution of the expectation values of operators acting on single molecules and on a discrete set of special modes in an, in principle, exact way. Although in practice it is impossible to evaluate these equations rigorously, it is possible to perform a perturbation expansion, which systematically incorporates dynamic correlations and interactions. There are a number of advantages to our approach. First, its application is not limited to the special case of the lattice, which we chose in this paper; more general systems such as concentrated solutions, doped crystals, and aggregates may be treated in a similar manner. Second, this procedure does not address external fields but instead is formulated directly in terms of the internal electromagnetic fields. Therefore a conversion of external susceptibilities to the actual internal ones is not needed. Third, an equation-of-motion approach makes it possible to treat collective effects of matter and radiation field (polariton effects).

Using the multipolar Hamiltonian, we exactly recovered Maxwell's equations for the radiation field. Furthermore, the reduced equations of motion for the material variables to second order in the molecular dipole μ coincide with the optical Bloch equations in the local-field approximation. The local field is a mean-field concept that is frequently used in the treatment of optics in condensed phases but was never derived from first principles. Our procedure yields the approximation as a lowest-order result and, moreover, shows how to improve on it systematically. The expression for the local field that is found from our approach explicitly contains the retarded intermolecular dipole–dipole interactions, and the equations of motion properly account for the effects of radiative self-interactions and superradiance. Reduced equations of motion may also be obtained by using the minimal coupling Hamiltonian, but these equations will not assume the form of the optical Bloch equations, and it is impossible to identify a local field in them.

The Bloch equations in the local-field approximation provide an easy means of evaluating linear and nonlinear susceptibilities for condensed media, as described in the last paragraph of Section 3. In this paper we particularly studied the dielectric function that follows from the linearized Bloch equations and compared it with the well-known result obtained by Hopfield in his treatment of polaritons.[12] The most important difference between the two expressions is the presence of radiative damping and a level shift in our result. A further difference is the signature of the retarded intermolecular dipole–dipole interactions in our result as opposed to the instantaneous interactions in Hopfield's expression. This provides a means of assessing the importance of retardation effects, and from the detailed quantitative study that we presented in Section 4 it may be concluded that for typical systems these effects on the dielectric function are negligible. Hopfield's result was obtained by using the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian and may be derived by evaluating the reduced equations of motion within this Hamiltonian, discarding the kernel totally. However, in view of earlier results on intermolecular interactions mediated by photons,[34,35] we are convinced that in the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian the kernel term to order μ^2 would also generate the retarded intermolecular interactions (while canceling the instantaneous ones) and yield radiative decay rates and level shifts. Even in this higher-order approximation, the equations would not have the form of the Bloch equations; these can be obtained only from a $\mu \cdot \mathbf{D}$ type of Hamiltonian.

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